THE STEREOCHEMISTRY OF INORGANIC COMPLEX COMPOUNDS

I. REACTIONS OF DICHLORODIETHYLENEDIAMINE COBALTIC CHLORIDE WITH NITRITES

II. THE STEREOISOMERS OF DICHLORODIETHYLENEDIAMINE PLATINIC CHLORIDE

BY

BETTY RAPP

B.S., University of Toledo, 1935
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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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THE STEREOCHEMISTRY OF INORGANIC COMPLEX COMPOUNDS

I. REACTIONS OF DICHLORODIETHYLENEDIAMINE COBALTIC CHLORIDE WITH NITRITES

It was Werner's [1] belief that the mechanism involved in a Walden inversion occurring in organic compounds is essentially the same as that involved in a *cis-trans* rearrangement occurring in inorganic complex compounds. This concept may be applied to dichlorodiethylenediamine cobaltic complexes by assuming that, in starting with a compound of *cis* configuration, the formation of a *trans* product as a result of a substitution reaction is due to the loosening of the nitrogen-cobalt linkage *trans* to the chloro group not involved in the actual substitution. This nitrogen atom then assumes the position vacated by the chloro group being replaced, and the entering group takes the position previously occupied by the nitrogen atom. If, on the other hand, the linkage of the nitrogen *cis* to the non-reacting chloro group is loosened during the replacement reaction, a Walden inversion occurs and the product has a *cis* configuration enantiomorphous with that of the starting compound. There is, of course, the possibility that the substituting group may take the very position vacated by the replaced group, although this is contrary to the theory of Olsen [2] which states that, for organic compounds, every step in a substitution reaction involves an inversion.

On the basis of this interpretation of Werner's theory it would seem that in any substitution reaction either a *cis-trans* rearrangement or a Walden inversion might occur, but not both. Also, if the reaction should involve direct replacement, there would be no chance of a *cis-trans* rearrangement, but conditions might be found which would permit a Walden inversion. This is reasoning on the basis that all *cis* positions are equivalent and differently characterized from the *trans* position.

In order to test this theory a study was made of the replacement of one and both chloro groups in the complex compound, dichlorodiethylenediamine cobaltic chloride, by nitro groups. Werner [3] had found that in converting the active dichloro complex to the active chloro nitro and dinitro derivatives, no *cis-trans* rearrangement and no racemization occurred. This, then, appears to be a substitution reaction involving actual direct replacement or its equivalent.

The action of sodium nitrite and of silver nitrite on freshly prepared and on aged solutions of the active dichloro compound resulted in the production of *dextro* rotatory nitro derivatives. Evidence is cited which indicates that these products have the same configuration as that of the starting compound. These are slow reactions involving the formation of intermediate aquo compounds. Attempts to force the reaction to proceed in a single step by using large excesses of reagent according to the method of Bailar and McReynolds [4] caused the intermediate formation of a *dextro* rotatory dinitrito derivative which slowly rearranged to the *dextro* dinitro compound. Since no inversion could be demonstrated, it appears that substitution of chloro or aquo groups by nitro groups in diethylenediamine cobalt complexes involves only simple, direct substitution.

The reconversion of the active dinitro compound to the active dichloro derivative by concentrated hydrochloric acid is described. This reaction also involves no inversion.

II. THE STEREOISOMERS OF DICHLORODIETHYLENEDIAMINE PLATINIC CHLORIDE

Syntheses of *cis* and *trans* dichlorodiethylenediamine platinic chloride are described. Platinous chloride is prepared by the reduction of chloroplatinic acid with sulfur dioxide. The platinous chloride is dissolved in ethylenediamine, and diethylenediamine platinous chloride is crystallized from the resulting solution. Chlorination of this compound yields the white dihydrate of *trans* dichlorodiethylenediamine platinic chloride. This is converted to carbonato diethylenediamine platinic carbonate by grinding with moist silver carbonate. Treatment of the carbonato salt with alcoholic hydrogen chloride yields two products. The chief product is the yellow anhydrous *cis* dichlorodiethylenediamine platinic chloride. The other product, a deep-red compound of great solubility, results from the partial reduction of the carbonato salt by the alcoholic hydrogen chloride and has the empirical formula, $Pt\,en_2\,Cl_3 \cdot H_2O$. Since the appearance and behavior of this salt correspond closely to those of certain tetraethylamine derivatives of trivalent platinum described by Drew and Tress,[5] it has been assigned the formula, $[Pt\,en_2\,Cl\,H_2O]\,Cl_2$.

The *cis* dichloro salt is converted to the less soluble *trans* modification by the action of hydrochloric acid. Unsuccessful attempts to resolve it are reported.

The preparation of tetrachloromonoethylenediamine platinum and of dibromodiethylenediamine platinic bromide are described.

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VITA

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